

Supporting Information

Preparation of Highly Thermally Conductive Polymer Composite at Low Filler Content via a Self-assembly Process between Polystyrene Microsphere and Boron Nitride Nanosheet

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Experimental details

1. Materials

Isopropanol, ethanol, polyvinyl pyrrolidone (PVP, $M_w=40000$) were purchased from Shanghai chemical Corp. Styrene (St), ammonium peroxodisulphate (APS) and poly(dislyldimethylammonium chloride) (PDDA) were supplied by Aladdin. Boron nitride powder (BN) was purchased from Alfa Aesar. The polymerization inhibitor was removed from the styrene by infiltration through Al_2O_3 column. Deionized water was used for all experiments.

2. Preparation of polystyrene microspheres

For the typical preparation, 12.0 g of styrene, 0.09g of PVP, 18 ml of H_2O were firstly dissolved in ethanol (150 ml) in 500 ml three-neck round bottom flask. After purging with nitrogen for 30 min, the reactor was submerged in an oil bath and the polymerization was carried out at 70 °C for 12 h.

3. Liquid exfoliation of BN

5.0 g of hexagonal BN powders were dispersed into 500 ml isopropyl alcohol (IPA) and then sonicated for 18 h to exfoliate BN power by a sonicator (KQ5200DB) with an output power of 250 W. Then, the dispersion was centrifuged for 30 min at 1000 rpm to separate the non-exfoliated BN, obtaining the BNNS/IPA dispersion (0.5 mg/ml).

4. Characterization

The Transmission electron microscopy (TEM) experiments were conducted on JEOL JEM2011 F Microscope (Japan) operated at 200 kV. Scanning electron

microscopy (SEM) images were obtained on Zeiss Ultra 55 with EDX. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA 1 (Switzerland) from 100 to 800 °C in the nitrogen with a heating rate of 20 °C/min. XRD patterns were recorded on X'pert PRO PANalytical (Netherland) with Ni-filtered Cu K α radiation (40 kV, 40 mA). Atomic force microscopy (AFM) images were obtained using a Bruker Multimode 8 (Germany) in the tapping mode. Zeta potential was investigated on Zetasizer Nano-ZS90 (England). The glass transition temperature (T_g) and the specific heat (c , J g⁻¹ K⁻¹) were measured on differential scanning calorimeter (DSC) of TA Q2000 (American). The tensile curves of the composites were measured on a universal electronic tensile machine UTM4000 (SUNS, China). Volume resistivity of the composites was measured on a Keithley Electrometer. The in-plane and through-plane thermal diffusivity (α , m² s⁻¹) of the composites were detected by using a laser-flash diffusivity instrument LFA 447 (NETZSCH, Germany). Before the measurement, the square samples (1 mm×1 mm×0.25 mm) for through-plane thermal conductivity measurement and the circular samples (Ø25 mm×0.25 mm) for in-plane thermal conductivity measurement were firstly spray-coated with a thin layer of fine graphite powder at both sides. The density (ρ , g cm⁻³) of a specimen was calculated by the equation: $\rho=m/v$ and the eventual thermal conductivity (λ , W m⁻¹ K⁻¹) was calculated by the equation: $\lambda=\alpha \times c \times \rho$. The densities of BNNS and PS are 2.11 g cm⁻³ and 1.04 g cm⁻³, respectively.

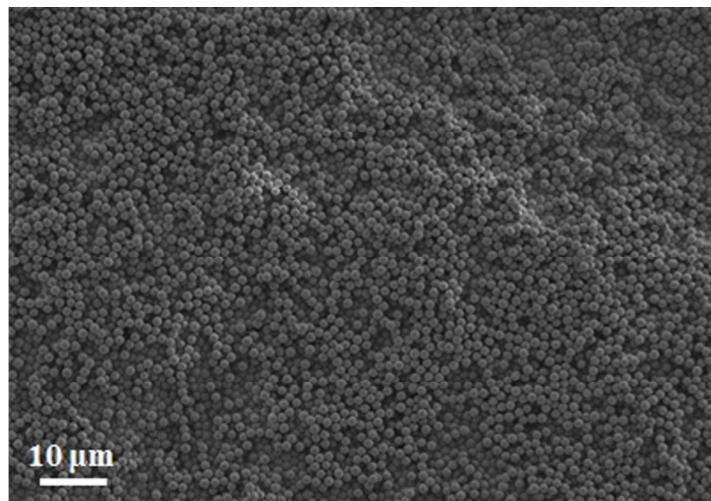


Figure S1 SEM images of the synthesized PS microspheres

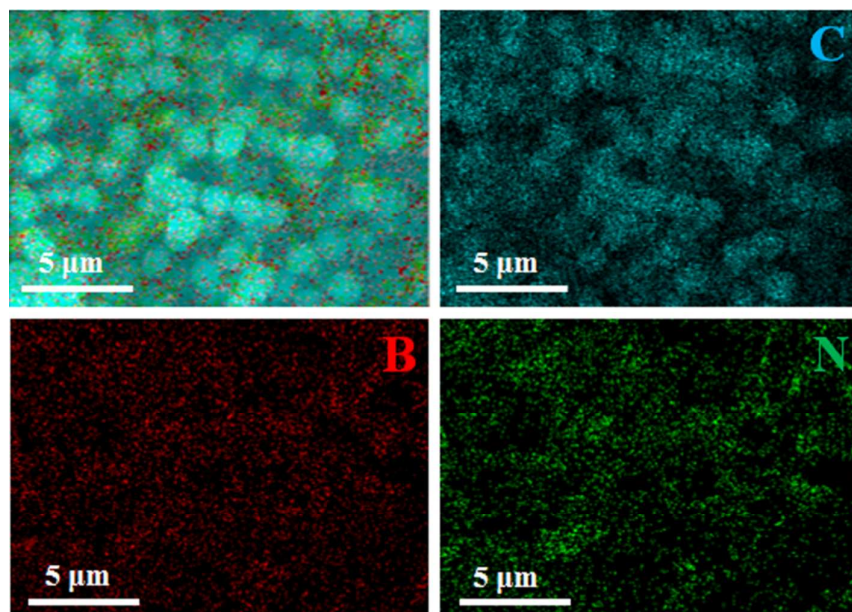


Figure S2 EDX elemental mapping images of the PS-BNNS complex microspheres

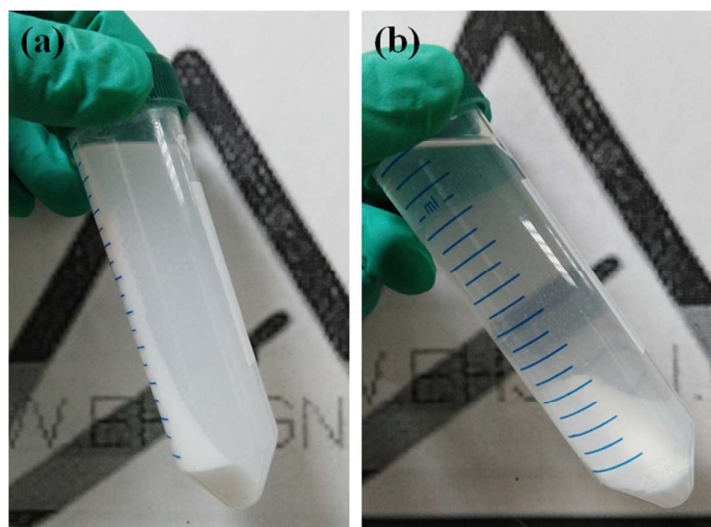


Figure S3 Photographs of the supernatant of PS-BNNS complex microspheres dispersion after centrifugation: (a) 15.6 vol% BNNS, (b) 13.4 vol% BNNS.

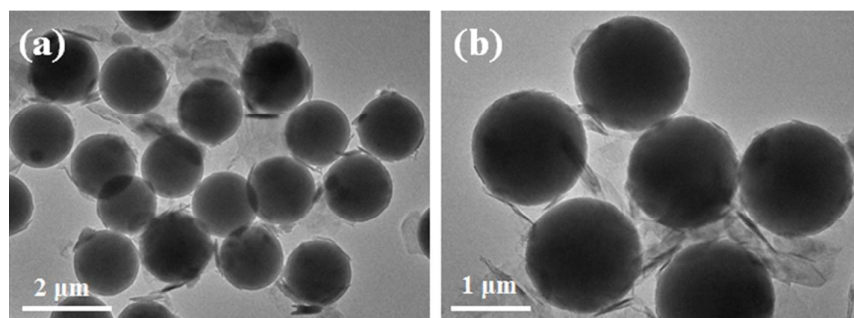


Figure S4 (a, b) TEM images of PS-BNNS complex microspheres with BNNS content of 13.4 vol%.

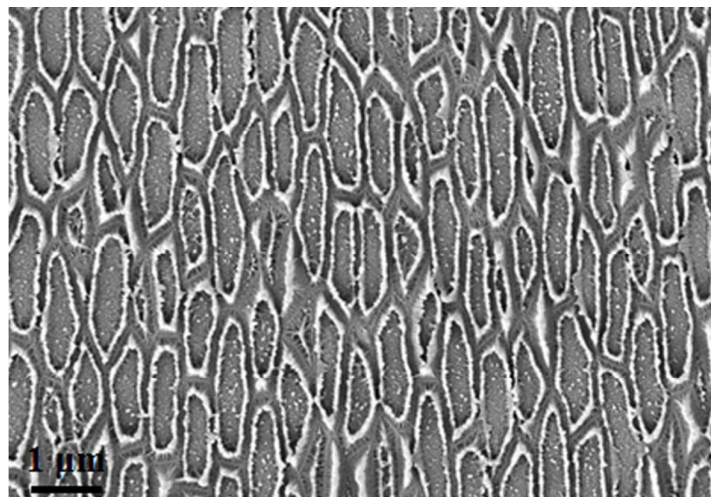


Figure S5 Enlarged cross-section image of pure PS composite.

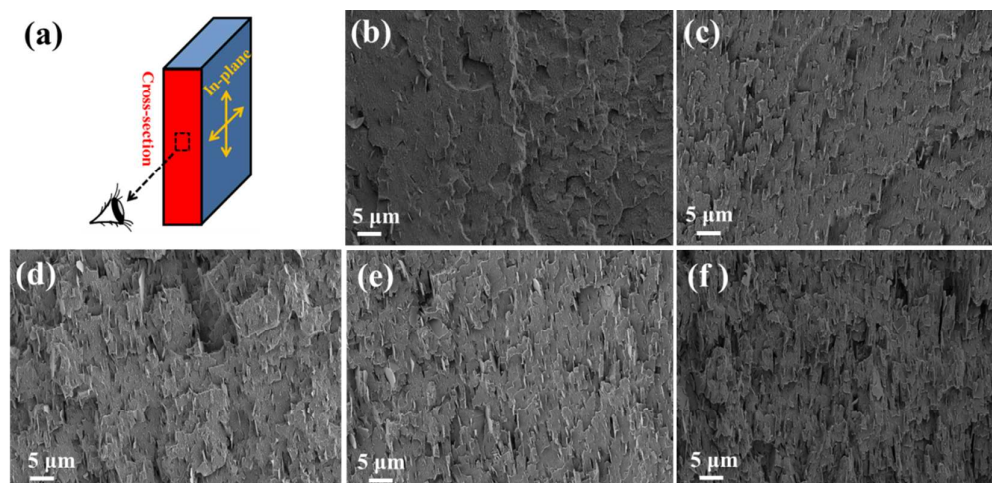


Figure S6 (a) Schematic illustration of the observation for the cross-section of PS/BNNS composite. Cross-section SEM images of PS/oriented BNNS composites with different BNNS loading: (b) 3.0 vol%, (c) 5.9 vol%, (d) 8.5 vol%, (e) 11.1 vol% and (f) 13.4 vol%

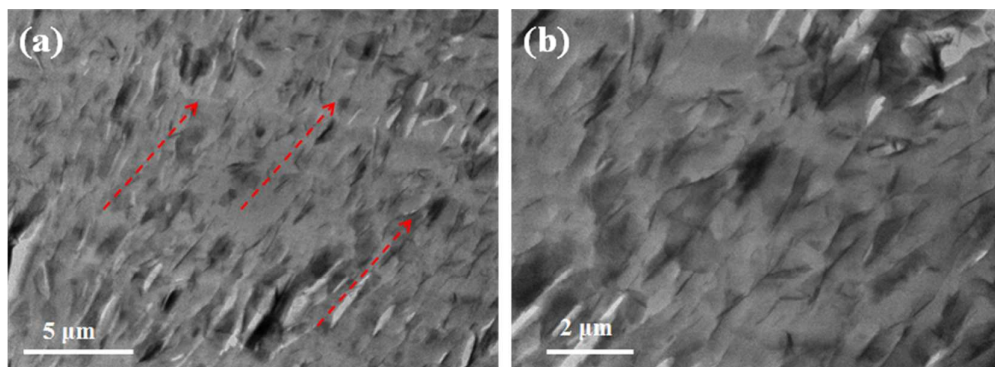


Figure S7. (a, b)TEM images of cross-sections of PS/oriented BNNS-13.4 composite.

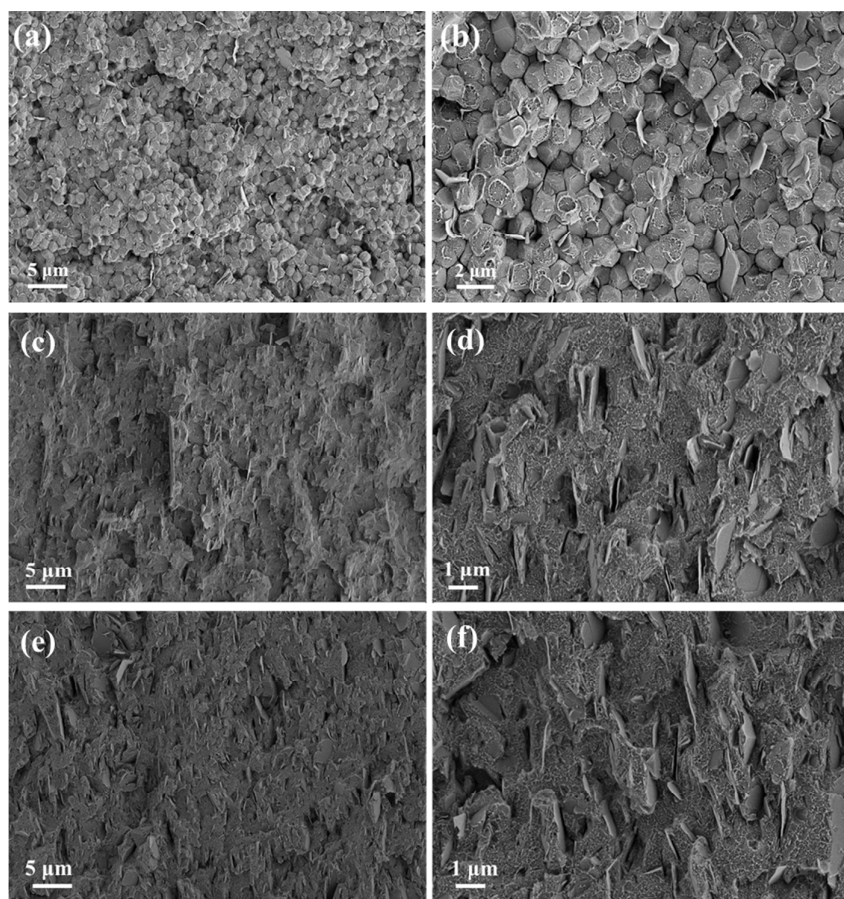


Figure S8. Fractured cross-sections of the PS/oriented BNNS-13.4 composite prepared at 80 °C (a, b), 150 °C (c, d) and 180 °C (e, f).

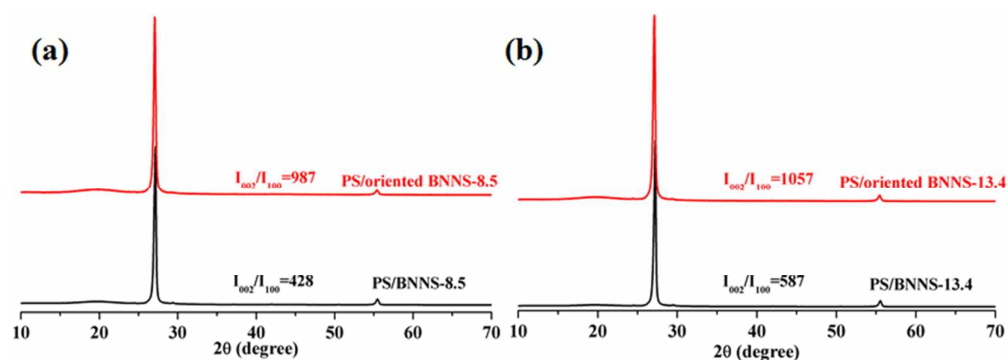


Figure S9 XRD patterns of the PS/oriented BNNS composites and PS/BNNS composites with different filler loading: (a) 8.5 vol%, (b) 13.4 vol%.

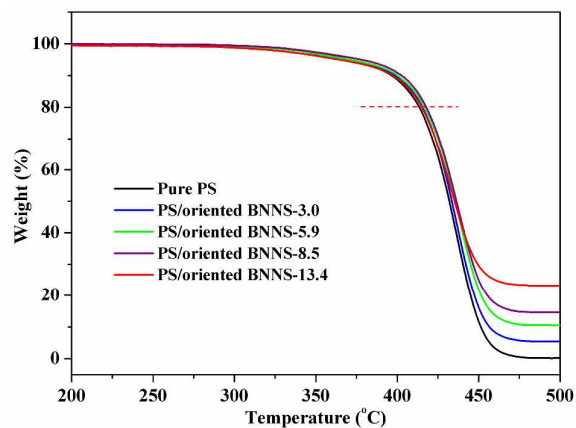


Figure S10 TGA curves of the PS/oriented BNNS composite with different BNNS loading

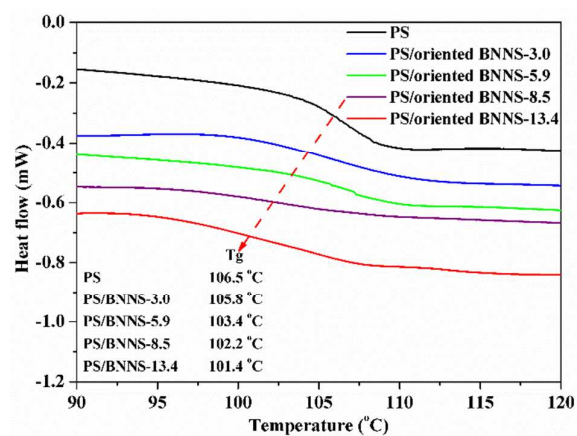


Figure S11 DSC curves of the PS/oriented BNNS composite with different BNNS loading

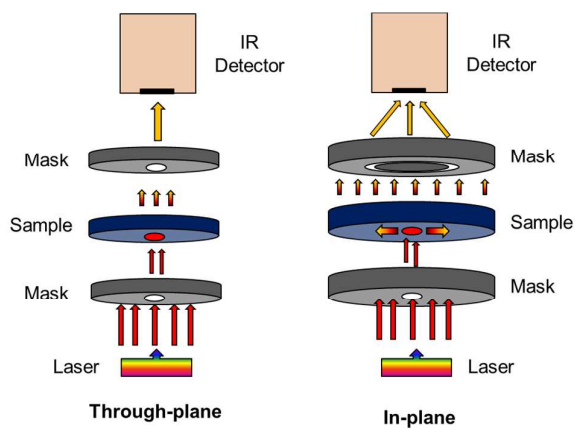


Figure S12 Schematic diagram of through-plane and in-plane thermal conductivity measurement by laser flash method.

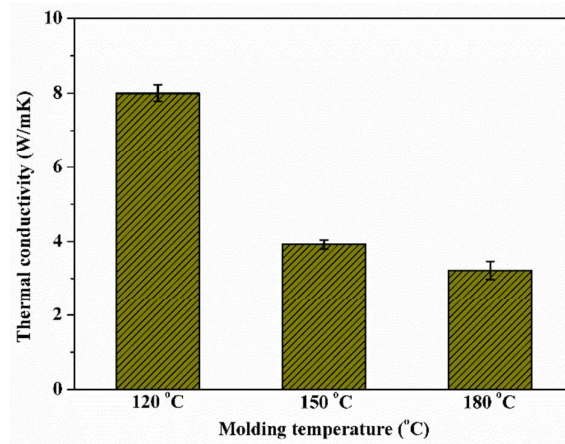


Figure S13 In-plane thermal conductivity of PS/oriented BNNS-13.4 composites hot-pressed at 120, 150 and 180 °C

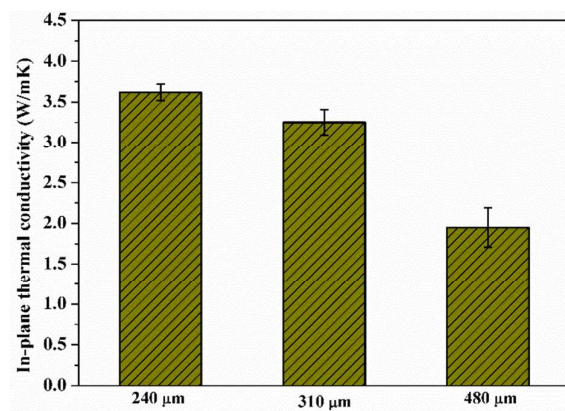


Figure S14 In-plane thermal conductivity of PS/oriented BNNS-8.5 composites with different thickness.

The through-plane conductivity measurement can adapt a wide sample thickness from 0.1 to 2 mm. Although the increased sample thickness will enhance the lateral heat loss, the provided computation model in LFA 447 would correct these lateral heat loss, finally obtaining a relatively accurate and steady thermal conductivity value. So the through-plane thermal conductivity is negligibly affected by the sample thickness in a wide range. While for the in-plane conductivity measurement, the heat flow must

go through two pathways, in-plane heat transfer and through-plane heat transfer, and then detected by the IR detector. Therefore, the sample thickness has a large influence on the heat loss. Large thickness will cause a large heat loss, especially for the material with high thermal conductivity anisotropy. Because the heat transfer in-plane thermal conductivity measurement is very complicated, so the mathematical correction has many limitations. In order to obtain a more accurate in-plane thermal conductivity, the sample thickness should be as low as possible. Therefore, in practical measurement, when the sample thickness exceeds a certain value, the measured in-plane thermal conductivity might be largely dependent of the thickness.